



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 :  C11D 3/50, 3/37		A1	(11) International Publication Number: WO 00/68352  (43) International Publication Date: 16 November 2000 (16.11.00)
<p>(21) International Application Number: PCT/EP00/03279</p> <p>(22) International Filing Date: 12 April 2000 (12.04.00)</p> <p>(30) Priority Data: 9910389.7 5 May 1999 (05.05.99) GB</p> <p>(71) Applicant (for all designated States except AU BB CA CY GB GD GH IE IL IN KE LK LS MN MW NZ SD SG SZ TT TZ UG ZA ZW): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).</p> <p>(71) Applicant (for AU BB CA CY GB GD GH IE IL KE LK LS MN MW NZ SD SG SZ TT TZ UG ZA ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London, Greater London EC4P 4BQ (GB).</p> <p>(71) Applicant (for IN only): HINDUSTAN LEVER LTD [IN/IN]; Hindustan Lever House, 165-166 Backbay Reclamation, Mumbai 400 020, Maharashtra (IN).</p>		<p>(72) Inventors: ELMES, Alfred, Roy; 3 Paisley Avenue, Eastham, Merseyside L62 8DL (GB). FRASER, Stuart, B.; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW (GB). KHOSDEL, Ezat; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW (GB). MARTIN, Alexander; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW (GB). MARTIN, John, Robert; 16 Prenton Hall Road, Prenton, Birkenhead, Merseyside CH43 0RA (GB). SHERRINGTON, David, Collin; Finlarig, 10 Hawthorn Avenue, Glasgow, Central Scotland G66 4RA (GB).</p> <p>(74) Agent: KAN, Jacob, H.; Unilever N.V., Patent Department, P.O. Box 137, NL-3130 AC Vlaardingen (NL).</p> <p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>	
<p>(54) Title: LAUNDRY COMPOSITIONS</p> <p>(57) Abstract</p> <p>A composition for use in the rinsing of laundry contains particles with perfume located or absorbed in or on the particles, characterised in that the particles are formed of cross-linked organic polymeric material that have a mean particle size not greater than 1 micron. The composition is preferably a fabric softener. A method of treating laundry with the composition is also provided.</p>			

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**LAUNDRY COMPOSITIONS**

This invention relates to the perfuming of rinse conditioner compositions.

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Rinse conditioners are products which are designed to be added to water used for the rinsing of laundry after washing with a detergent composition. Such conditioners contain a material whose function is to confer a benefit to 10 the laundry after the laundry has been rinsed and dried. One of the main benefits delivered by such products is softness.

It is normal to include perfume in such rinse conditioners, 15 firstly to enhance the attractiveness of the product to a user, and secondly to deliver the perfume to the laundry itself.

It is known to incorporate perfume into a porous carrier to 20 reduce the rate at which the perfume evaporates and hence extend the time during which the perfume fragrance remains perceptible.

US-A-4446032 discloses rinse conditioner compositions which 25 contain perfume trapped within carrier particles which may be porous or alternatively may be closed capsules with an impervious layer surrounding the perfume. This document teaches that a suspending agent should be included in the composition.

30

JP-A-63/122796 discloses the addition of a polymer latex which contains cationic or tertiary amino groups to a

detergent composition, for the purpose of enhancing perfume deposition.

WO98/28396 (Quest) discloses perfume absorbed within 5 organic polymer particles and which have a further polymer at their exterior. The polymer particles disclosed desirably have an average particle size of at least 10  $\mu\text{m}$ .

WO 98/28339 (Quest) discloses polymer particles comprising 10 a hydrophobic organic matrix and located at the exterior free cationic groups and a further polymer which comprises free hydroxy groups. The polymer particles disclosed desirably have an average particle size of at least 10  $\mu\text{m}$ .

15 EP 397 246 (Minnesota Mining) discloses perfume particles comprising perfume dispersed within certain water-insoluble polymeric materials and encapsulated in a protective shell by coating with a friable coating material.

20 EP 617 051 (Allied Colloids) discloses that the controlled release of a fragrance can be provided by incorporating it during emulsion polymerisation of water insoluble monomeric material in which it is dissolved, and by controlling the monomer blend composition and the Tg of the resultant 25 polymer.

The present invention provides a composition for use in the rinsing of laundry, containing particles with perfume located or absorbed in or on the particles, wherein the 30 particles are formed of cross-linked organic polymeric material and have a mean particle size not greater than 1 micron.

Preferably the polymeric material is a latex.

We have found that cross-linked latices give superior delivery of perfume to fabrics and better physical 5 stability to the product

In preferred forms, this invention is concerned with rinse conditioner compositions which incorporate a material effective to soften fabrics.

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Thus, according to an aspect of this invention there is provided a rinse conditioner composition containing a material effective to soften fabrics, and particles with perfume located or absorbed in or on the particles, 15 characterised in that the particles are formed of cross-linked organic polymeric material, and have a mean particle size not greater than 1 micron.

Incorporating perfume in this way can lead to an increase 20 in the amount of perfume which remains with the fabric after drying, especially when the fabric is dried in a heated tumble dryer.

Additionally particles of this small, colloidal size remain 25 suspended in an aqueous liquid and there is no need to incorporate a separate suspending agent.

In further aspect this invention provides the use of particles of cross-linked organic polymeric material with a 30 mean particle size of not greater than 1 micron and with perfume absorbed therein, in a rinse conditioner.

A method of treating laundry comprising contacting said laundry with a composition as herein described is also provided.

5 Furthermore, this invention provides a method of making a rinse conditioner which comprises mixing (i) a fabric softening material and (ii) particles of cross-linked organic polymeric material with a mean particle size not greater than 1 micron and with perfume located or absorbed 10 therein or thereon.

In this aspect, the invention can provide a way to incorporate perfume into a rinse conditioner composition while avoiding or mitigating adverse effects on viscosity.

15 We have found that perfume can produce adverse changes to the viscosity of rinse conditioner compositions, especially when these contain a substantial percentage of fabric softener. In extreme cases the addition of perfume to a concentrated rinse conditioner composition can cause it to 20 gel and become immobile.

Incorporation of perfume in a latex can avoid or mitigate this. This feature of the invention has been found to be applicable in particular to compositions which contain at 25 least 8%, more especially at least 12% by weight of fabric softening material. The amount of fabric softening material may lie in a range from 12% to 40% by weight or may be even greater up to 80% or 90% by weight of the composition.

30 It is here envisaged in particular that the fabric softening material may be cationic fabric softening material in an amount which is at least half of the total

quantity of fabric softening material present and in addition is at least 8% by weight of the composition, especially at least 12% by weight of the composition.

5 In certain preferred forms, this invention is particularly concerned with cross-linked polymer latices whose particles have the perfume trapped therein. We have found that cross-linked latices give superior delivery of perfume to fabrics and better physical stability to the product.

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Therefore, in a further aspect, this invention provides a product for use in the rinsing of laundry, containing perfume trapped within particles of an organic cross-linked polymeric latex, whose particles have a mean particle size 15 not greater than 1 micron.

Compositions in which this invention may be applied and materials used, will now be discussed in more detail.

20 Fabric Softening Rinse Conditioners

A variety of materials are effective to soften fabrics and can be delivered to fabric from an aqueous composition.

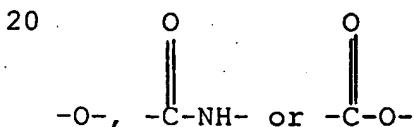
A fabric-softening agent functions to give fabric a softer 25 handle. Frequently such agents also provide an anti-static benefit.

Fabric softening agents used in rinse conditioner compositions are usually materials with low solubility in 30 water. Typically the solubility in acidified water at pH 2.5 and 20°C is less than 10g/litre, preferably less than 1g/litre. When added to rinse water such materials form a

dispersed phase which is then able to deposit on fabrics which are being rinsed in the water.

Many fabric softening materials fall within the categories 5 of amphoteric, zwitterionic, cationic and nonionic compounds.

Amphoteric, zwitterionic and cationic fabric softening materials include a polar group and usually one or more 10 hydrophobic aliphatic chains such as alkyl or alkenyl groups each of which contains at least 6 carbon atoms, e.g. a range from 6 to 50 carbon atoms in a continuous hydrocarbon chain or a hydrocarbon chain interrupted by a 15 heteroatom. In many such materials there are either a single aliphatic chain containing 12 to 50 carbon atoms, or a plurality of aliphatic chains each containing 6 to 30 carbon atoms. Such aliphatic chains may be interrupted by 20 a heteroatom as for instance in an



linkage. Generally it is preferred that a hydrophobic 25 aliphatic chain does not incorporate more than one interrupting heteroatom.

A nonionic fabric softening material will generally include a polar group and an aliphatic hydrocarbon chain of 6 to 30 30 carbon atoms, optionally interrupted by a heteroatom as mentioned above, although hydrocarbon chains of 6 to 18,

carbon atoms especially 6 to 11 carbon atoms are preferably without any interruption.

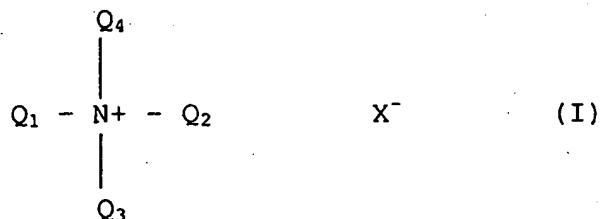
Cationic fabric softeners are of special commercial importance and are a preferred type of softener according to the invention. Preferred forms of this invention include cationic fabric softener, optionally with nonionic, amphoteric or zwitterionic fabric softener present in addition. Thus the amount of cationic fabric softening agent may be equal to, or greater than, the amount of any softening agent or surfactant which is not cationic.

Many commercially important fabric softening agents are organic compounds containing nitrogen, and at least one hydrocarbon chain of 6 to 50 carbon atoms. The nitrogen atom may well be quaternary, but need not be, as for example in amines and imidazolines which protonate to a quaternary form in acidic solution.

20 Some specific instances of fabric softening agents are:

1) Acyclic quaternary ammonium compounds. These compounds are of the general formula (I)

25



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wherein each  $Q_1$  is a hydrocarbyl group containing from 15 to 22 carbon atoms.  $Q_2$  is a saturated alkyl or hydroxy

alkyl group containing from 1 to 4 carbon atoms.  $Q_3$  may be as defined for  $Q_1$  or  $Q_2$  or may be phenyl,  $Q_4$  may be defined as for  $Q_1$  or  $Q_2$ , and  $X^-$  is an anion preferably selected from halide, acetate, methyl sulphate and ethyl sulphate  
5 radicals.

Throughout this discussion of fabric softening agents the expression hydrocarbyl group refers to alkyl or alkenyl groups optionally substituted or interrupted by functional  
10 groups such as -OH, -O-, CONH, -COO-, etc.

Representative examples of these quaternary softeners include tallow trimethyl ammonium methyl sulphate or chloride; ditallow dimethyl ammonium chloride; ditallow  
15 dimethyl ammonium methyl sulphate; dihexadecyl dimethyl ammonium chloride; di(hydrogenated tallow) dimethyl ammonium methyl sulphate or chloride; di (coconut) dimethyl ammonium chloride dihexadecyl diethyl ammonium chloride; dibehenyl dimethyl ammonium chloride.

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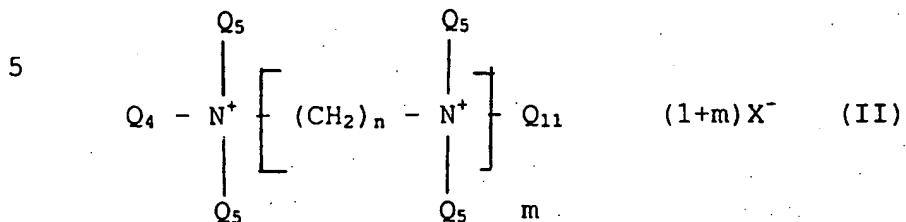
Preferred among these are ditallow dimethyl ammonium chloride, di (hydrogenated tallow) dimethyl ammonium chloride, di(coconut) dimethyl ammonium chloride and di(coconut) dimethyl ammonium methosulphate.

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Examples of commercially available materials in this class are ARQUAD 2C, ARQUAD 2HT, ARQUAD 2T (all ex Akzo), PRAPAGEN WK, PRAPAGEN WKT, DODIGEN 1829 (all ex Clariant), QUERTON 4BG, QUERTON 442 (all ex Akzo), AMMONYX KP, AMMONYX  
30 SKD (all ex Millchem), SYNPROLAM FS ( ex Unichema). The product names are believed to be trademarks.

## 2) Alkoxylated Polyamines

Alkoxylated polyamines of general formula (II) are known



10 Each  $\text{Q}_4$  is a hydrocarbyl group containing from 10 to 30 carbon atoms. The  $\text{Q}_5$  groups may be the same or different each representing hydrogen,  $(-\text{C}_2\text{H}_4\text{O})_p\text{H}$ ,  $(\text{C}_3\text{H}_6\text{O})_q\text{H}$ ,  $(\text{C}_2\text{H}_4\text{O})_p$ ,  $(\text{C}_3\text{H}_6\text{O})_q\text{H}$ , and alkyl group containing from 1 to 3 carbon atoms or the group  $(\text{CH}_2)_n\text{N}(\text{Q}_5)_2$ ;  $n$  and  $n'$  are each an

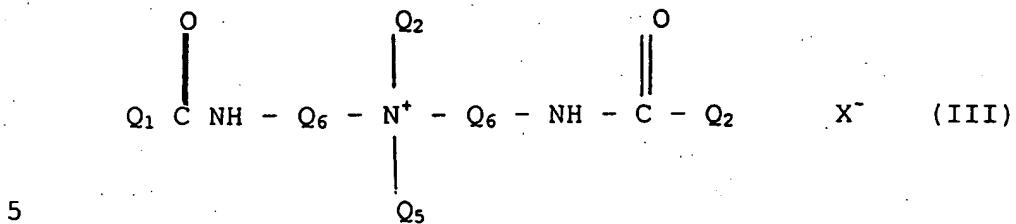
15 integer from 2 to 6,  $m$  is an integer from 1 to 5 and  $p$ ,  $q$  and  $(p' + q')$  may be numbers such that  $(p + q + p' + q')$  does not exceed 25.  $\text{X}^-$  is an anion.

Alkoxylated polyamines suitable for use herein include N-  
 20 tallowyl, NN'N'-tris (2 hydroxethyl)-1,3- propane diamine di-hydro chloride; N-cocyl N,N,N',N' pentamethyl-1,3 propane diammonium dichloride or dimethosulphate; N-stearyl N,N',N' tris (2-hydroxyethyl) N,N1'dimethyl-1,3 propanediammonium dimethyl sulphate; N-palmityl N,N',N' tris (3-hydroxyproyl)-1,3-propanediammonium dihydrobromide; N-  
 25 tallowyl N-(3 aminopropyl)-1,3-propanediamine trihydrochloride.

## 3. Diamido Quaternary Ammonium Salts

30 Diamido quaternary salts of general formula (III) are also known to be useful as fabric softening agents.

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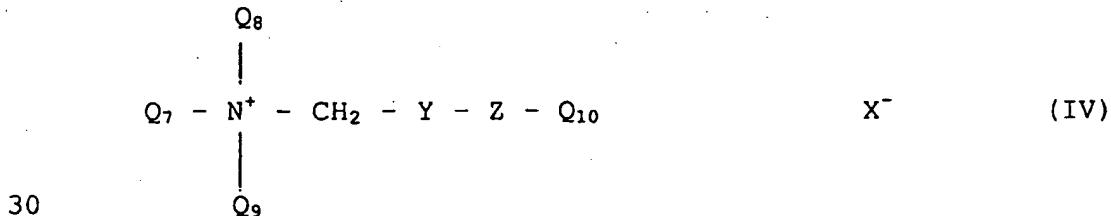
$\text{Q}_6$  is a divalent alkylene group containing from 1 to 3 carbon atoms.  $\text{Q}_1$ ,  $\text{Q}_2$ ,  $\text{Q}_5$  and  $\text{X}^-$  are as defined previously. Examples of suitable materials are methylbis

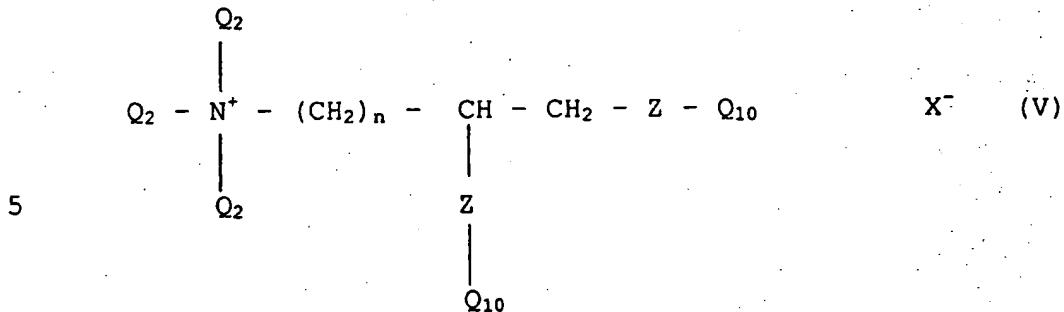
(tallowamidoethyl) (2-hydroxyethyl) ammonium methyl sulphate and methyl bis (hydrogenated tallowamido ethyl) (2-hydroxyethyl) ammonium methyl sulphate. These materials are available from Goldschmidt under trade names VARISOFT 222 and VARISOFT 110 respectively and under the trade name ACCOSOFT from Stepan.

#### 4. Ester Quaternary Ammonium Salts

A number of ester group containing quaternary ammonium salts, including those disclosed in EP 345842 A2 (Procter & Gamble), EP 239910 (Procter & Gamble) and US 4137180 (Lever) and incorporated herein by reference, are known to be particularly useful as softening materials. These materials can be represented by generic formulae (IV) and (V) below.

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In formula (IV)  $\text{Q}_7$  is a hydrocarbyl group containing 1 to 4 10 carbon atoms,  $\text{Q}_8$  is  $(\text{CH}_2)_n\text{-Z-Q}_{10}$  where  $n$  is an integer from 1 to 4 or  $-\text{Q}_{10}$ .  $\text{Q}_9$  is an alkyl or hydroxyalkyl group of 1 to 4 carbon atoms, or is as defined for  $\text{Q}_8$ .  $\text{Q}_{10}$  is a hydrocarbyl group containing from 12 to 22 carbon atoms and  $\text{Y}$  can be  $-\text{CH}(\text{OH})\text{-CH}_2\text{-}$  or  $\text{Q}_5$ , as previously defined.  $\text{Z}$  can 15 be  $-\text{O-C(O)-O}$ ,  $\text{C(O)-O}$  or  $-\text{O-C(O)-}$  and  $\text{X}^-$  is an anion.

In formula (V) the symbols  $\text{Q}_2$ ,  $\text{Q}_{10}$ ,  $\text{Z}$  and  $\text{X}^-$  have the meanings defined previously.

20 Examples of suitable materials based on formula IV are methyl bis-[ethyl(tallowyl)]-2-hydroxyethyl ammonium methyl sulphate (or its oleetyl equivalent),  $\text{N,N-di(tallowyl-oxyethyl)-N,N-dimethyl ammonium chloride}$ ;  $\text{N,N-di(2-tallowyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride}$ ; 25  $\text{N,N-di(2-tallowyloxyethylcarbonyl oxyethyl)-N,N-dimethyl ammonium chloride}$ ;  $\text{N-(2-tallowloxy-2-ethyl)-N-(2-tallowyl-oxo-2-oxyethyl)-N, N-dimethyl ammonium chloride}$ ;  $\text{N,N,N-tri(tallowyl-oxyethyl)-N-methyl ammonium chloride}$ ;  $\text{N-(2-tallowyloxy-2-oxyethyl)-N-(tallowyl-N,N-dimethyl)-ammonium chloride}$ . Tallowyl may be replaced with cocoyl, palmoyl, lauryl, oleyl, stearyl and palmityl groups. An illustrative 30

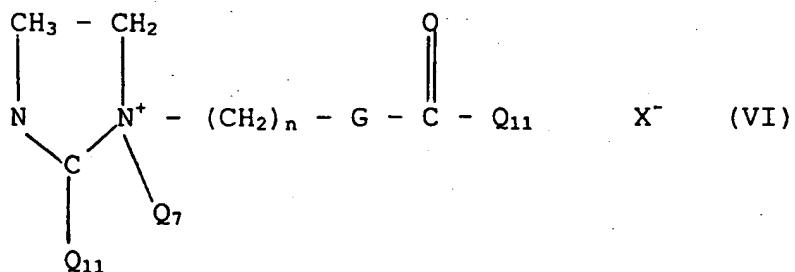
example of a formula V material is 1,2-(hardened) ditallowyloxy-3-trimethyl ammonium propane chloride.

Examples of commercially available materials can be obtained under the trade name STEPANTEX VRH 90 (ex Stepan), AKYPOQUAT (ex Kao) and as mixtures of mono and ditallow esters of 2,3-dihydroxy propane trimethyl ammonium chloride (ex Clariant).

#### 10 5. Quaternary Imidazolinium Salts

A further class of cationic softener materials is the imidazolinium salts of generic formula (VI).

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Wherein  $Q_{11}$  is a hydrocarbyl group containing from 6 to 24 carbon atoms, G is  $-N(H)-$ , or  $-O-$ , or  $NQ_2$ , n is an integer between 1 and 4, and  $Q_7$  is as defined above.

25

Preferred imidazolinium salts include 1-methyl-1-(tallowylamido) ethyl-2-tallowyl-4,5 dihydro imidazolinium methosulphate and 1-methyl-1-(palmitoylamido) ethyl-2-octadecyl-4,5-dihydroimidazolinium chloride. Other useful imidazolinium materials are 2-heptadecyl-1-methyl-1-(2 stearylamido) ethyl imidazolinium chloride and 2-lauryl-1-hydroxyethyl-1-olayl imidazolinium chloride. Also suitable

are the imidazolinium fabric softening components of US 4127489 incorporated here by reference.

Representative commercially available materials are VARISOFT 475 (ex Goldschmidt) and REWOQUAT W7500 (ex Rewo).

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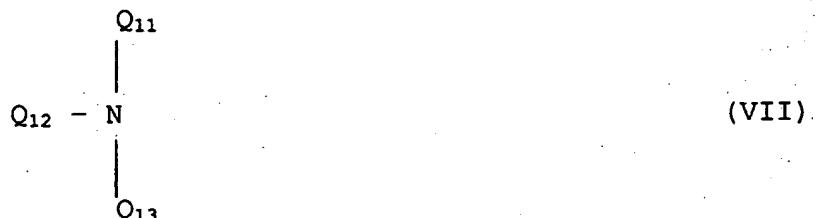
A particular aspect of the invention relates to compositions wherein the amount of fabric softening material which is cationic is a majority of the fabric softening material present.

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#### 6. Primary Secondary and Tertiary Amines

Primary, secondary and tertiary amines of general formula (VII) are useful as softening agents.

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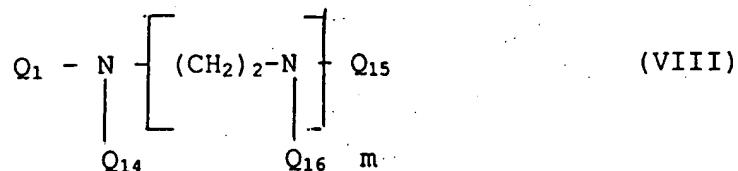


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wherein  $Q_{11}$  is a hydrocarbyl group containing from 6 to 24 carbon atoms,  $Q_{12}$  is hydrogen or a hydrocarbyl group containing from 1 to 22 carbon atoms and  $Q_{13}$  can be 25 hydrogen or  $Q_7$ . Preferably amines are protonated with hydrochloric acid, orthophosphoric acid or citric acid or any other similar acids for use in fabric conditioning compositions of this invention.

#### 30 7. Alkoxylated Amines

Alkoxylated amines of general formula (VIII) are also useful as components of this invention.



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wherein  $Q_{14}$  is  $(C_2H_4O)_xH$ ,  $Q_{15}$  is  $(C_2H_4O)_yH$  and  $Q_{16}$  is  $(C_2H_4O)_zH$  and  $x+y$  is within the range 2 to 15 and  $x+y+z$  is within the range 3 to 15,  $m$  can be 0, 1 or 2 and  $Q_1$  is as previously defined.

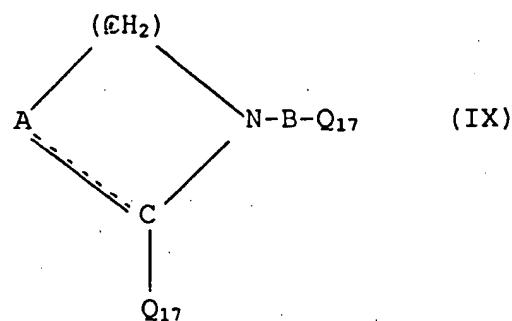
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Examples of these materials are monotallowdipolyethoxyamine containing from 2 to 30 ethylene oxide units, tallow N, N', N' tris (2-hydroxyethyl)-1,3 propylene diamine or C<sub>10</sub> to C<sub>18</sub> alkyl-N-bis(2-hydroxyethyl) amines.

15 Examples of commercially available materials are available under the trade names ETHOMEEN and ETHODUOMEEN (ex Akzo).

## 8. Cyclic Amines

Other useful materials are dialkyl cyclic amines  
20 represented by formula (IX).



30 wherein the groups  $Q_1$  are independently selected from hydrocarbyl groups containing from 3 to 30 carbon atoms and A can be oxygen (-O-) or nitrogen (-N-), preferably

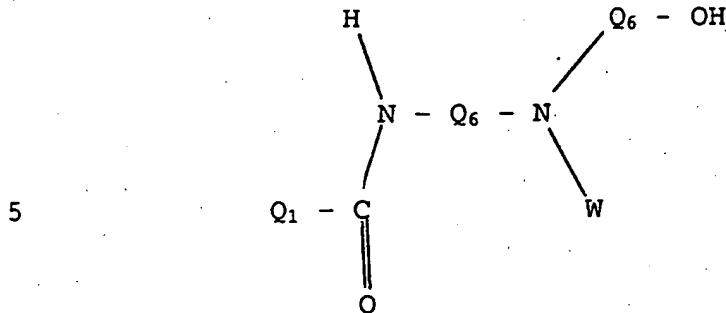
nitrogen; B is selected from Q<sub>5</sub> as defined earlier or the group -Q<sub>13</sub>-T-C(O) - where Q<sub>18</sub> is either Q<sub>5</sub> or (-C<sub>2</sub>H<sub>4</sub>O)<sub>m</sub> with m being an integer from 1 to 8 and T being selected from oxygen or NQ<sub>13</sub>. The broken line shows a possible double bond between A and C. If absent, it is replaced by bond(s) to additional hydrogen(s).

Illustrative materials are 12-stearyl oxyethyl-2-stearyl imidazoline, 1-stearyl oxyethyl-2-palmityl imidazoline, 1-10 stearyl oxyethyl myristyl imidazoline, 1-palmityl oxyethyl-2-palmityl imidazoline, 1-palmityl oxyethyl-2-myristyl imidazoline, 1-stearyl oxyethyl-2-tallow imidazoline, 1-myristyl oxyethyl-2-tallow imidazoline, 1-palmityl oxyethyl-2-tallow imidazoline, 1-coconut oxyethyl-2-coconut 15 imidazoline, 1-tallow oxyethyl-2-tallow imidazoline and mixtures thereof. Also useful is stearyl hydroxyethyl imidazoline, available commercially as MONAZOLINE S (ex Unichema), 1-tallow amido ethyl-2-tallow imidazoline and Methyl-1-tallow amidoethyl-2-tallow imidazoline.

20

Yet another class of suitable fabric softening materials are the condensation products formed from the reaction of fatty acids with a polyamine selected from the group consisting of hydroxyalkyl, alkylene diamines and 25 dialkylenetriamines and mixtures thereof. Suitable materials are disclosed in EP-A-199382 (Procter). Preferred among these are mixtures of molecules of the generic formula X and corresponding salts obtained by partial protonation.

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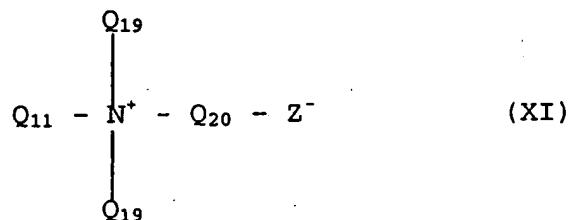


10 W is selected from hydrogen and the group  $-C(O)-Q_1$  and other symbols are as previously defined. Commercially available materials of this class can be obtained from Clariant as Ceranine HC39, HCA and HCPA.

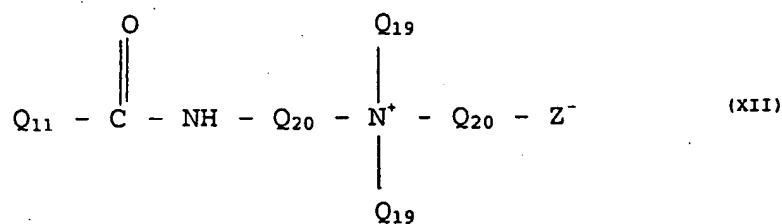
15 9. Zwitterionic Fabric Softeners

Other useful ingredients of softening systems include zwitterionic quaternary ammonium compounds such as those disclosed in EP 332270 A2 (Unilever) incorporated herein by reference. Representative materials in this class are 20 illustrated by general formula (XI) and (XII).

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wherein the groups  $Q_{19}$  are selected independently from  $Q_7$ ,  $Q_{11}$  and  $Q_{14}$ ;  $Q_{20}$  is a divalent alkylene group containing 1 to 3 carbon atoms and may be interrupted by  $-O-$ ,  $-CONH-$ ,  $-C(O)O-$ , etc; and  $Z^-$  is an anionic water solubilising group 5 (e.g. carboxy, sulphate, sulpho or phosphonium).

Examples of commercially available materials are the EMPIGEN CD and BS series (ex Albright & Wilson), the REWOTERIC AM series (ex Goldschmidt) and the Tegobetaine F, 10 H, L and N series (ex GOLDSCHMIDT).

In all of the aforementioned fabric softening compounds where an alkyl chain name is given, the hardened equivalent may also be used, for example tallow or hardened tallow.

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#### 10. Nonionic Ingredients

It is well known to blend nonionic material with cationic, amphoteric or zwitterionic softening materials as a means of improving dispersion of the product in rinse waters and 20 enhancing the fabric softening properties of the softener blend.

Suitable nonionic adjuncts include lanolin and lanolin derivatives, fatty acids containing from 10 to 18 carbon 25 atoms, esters of fatty acids containing from 8 to 24 carbon atoms with monohydric alcohols containing from 1 to 3 carbon atoms, and polyhydric alcohols containing 2 to 14 carbon atoms eg 2 to 12 carbon atoms such as sucrose, sorbitan, together with alkoxylated fatty acids, alcohols 30 and lanolins containing an average of not more than 7 alkylene oxide groups per molecule. Suitable materials have been disclosed in EP-A-88520 (Unilever), EP-A-122141

(Unilever), GB 2157728A (Unilever), GB 8410321 (Unilever), EP-A-159918 (Unilever), EP-A-159922 (Unilever) and EP-A-79746 (Procter).

5 The composition may additionally or alternatively comprise, as a fabric softening agent, an oily sugar derivative which is a liquid or soft solid derivative of a cyclic polyol or of a reduced saccharide, said derivative resulting from 35 to 100% of the hydroxyl groups in said polyol or in said 10 saccharide being esterified or etherified. The derivative has two or more ester or ether groups independently attached to a C<sub>8</sub>-C<sub>22</sub> alkyl or alkenyl chain. Preferably the oily sugar derivative contains 35% by weight tri or higher esters, eg at least 40%. W098/16538 (Unilever) discloses 15 such derivatives and is incorporated herein by reference.

Preferably 35 to 85% most preferably 45 to 70% of the hydroxyl groups in said cyclic polyol or reduced saccharide are esterified or etherified to produce the derivative.

20

The tetra etc prefixes used refer to the average degrees of esterification or etherification; the compounds exist as a mixture comprising the monoester to fully esterified ester.

25 The derivatives do not have substantial crystalline character at 20°C. The starting material is esterified or etherified with said alkyl or alkenyl chains to an extent so as to produce the derivatives as a liquid or soft solid.

30 Typically the derivative has 3 or more, preferably 4 or more, eg 3 to 5, ester or ether groups or mixtures thereof.

The derivative may be obtained from a saccharide, e.g. monosaccharides including xylose, arabinose, galactose, fructose, sorbose and especially glucose, or, disaccharides including maltose, lactose, cellobiose and especially 5 sucrose.

An example of a reduced saccharide is sorbitan. If based on a disaccharide it is preferred if the disaccharide has 3 or more ester or ether groups attached to it e.g. include 10 sucrose tri, tetra and penta esters.

Examples of suitable derivatives include esters of alkyl(poly)glucosides, in particular alkyl glucoside esters having a degree of polymerisation from 1 to 2.

15

The derivative may have branched or linear alkyl or alkenyl chains (of varying degrees of branching), mixed chain lengths and/or unsaturation. Those having unsaturated and/or mixed alkyl chain lengths are preferred.

20 For example, predominantly unsaturated fatty chains may be attached to the ester/ether groups, e.g. those derived from rape oil, cotton seed oil, soybean oil, oleic, tallow, palmitoleic, linoleic, erucic or other sources of unsaturated vegetable fatty acids.

25

Examples of suitable oily sugar derivatives include sucrose tetratallowate, sucrose tetrarapeate, sucrose tetraoleate, sucrose tetraesters of soybean oil or cotton seed oil, cellobiose tetraoleate, sucrose trioleate, sucrose 30 triapeate, sucrose pentaoleate, sucrose pentarapeate, sucrose hexaoleate, sucrose hexarapeate, sucrose triesters, pentaesters and hexaesters of soybean oil or cotton seed

oil, glucose trioleate, glucose tetraoleate, xylose trioleate, sucrose tetralinoleate or sucrose tetra-, tri-, penta- or hexa- esters with any mixture of predominantly unsaturated fatty acid chains.

5

Other oily sugar derivatives suitable include sucrose pentalaurate, sucrose pentaerucate, sucrose tetraerucate. Suitable materials include some of the Ryoto series available from Mitsubishi Kagaku Foods Corporation.

10

The liquid or soft solid derivatives are characterised as materials having a solid:liquid ratio of between 50:50 and 0:100 at 20°C as determined by  $T_2$  relaxation time NMR, preferably between 43:57 and 0:100, most preferably between 15 40:60 and 0:100, such as, 20:80 and 0:100. The  $T_2$  NMR relaxation time is commonly used for characterising solid:liquid ratios in soft solid products such as fats and margarines. For the purpose of the present invention, any component of the NMR signal with a  $T_2$  of less than 100 20 microsecond is considered to be a solid component and any component with  $T_2$  greater than 100 microseconds is considered to be a liquid component.

The oily sugar derivatives can be prepared by a variety of 25 methods well known to those skilled in the art. Typical preparations of these materials are disclosed in US 4 386 213 and AU 14416/88 (Procter and Gamble).

Fabric softening compositions generally do not contain 30 anionic detergent active nor bleach, nor detergency builder. It is desirable that the amounts (of any) of anionic detergent active, bleach and detergency builder are

all less than the amount of the fabric softening agent. The amount of each one of these may well be less than 5% by weight of the whole composition.

5 A rinse conditioner composition according to this invention will usually contain from 0.5% to 90% by weight of the fabric softening material, for example 0.5-40%. More specifically, so called dilute compositions generally contain from 1% to about 8% by weight of fabric softening

10 agent while compositions containing from about 8% up to 20% by weight of the fabric softening material have been classed as "concentrated". Higher concentrations, in the range of at least 8%, at least 12% or up to 40% by weight are also possible, but even this is not the upper limit.

15 Still higher concentrations from 40% up to 80% or even 90% by weight are possible in a very concentrated product. As mentioned above, either nonionic or cationic fabric softening agents may be used.

20 Perfume

The term "perfume" as used herein denotes materials which are used in perfumery and mixtures of such materials. Frequently the perfume will be a mixture of perfumery materials. Examples of suitable perfumes are to be found in

25 "Perfume and flavour Chemicals" by Steffen Erctander (Library of Congress Catalogue Card no. 75-91398).

The perfume may function solely to impart fragrance. However, perfumes can perform other functions, such as to

30 reduce the onset of body malodour as disclosed in US-A-4134838 and EP-A-545556. Such deodorant perfumes are within the scope of this invention and may or may not impart

fragrance. Deodorant perfumes with low perceptible odour are disclosed in EP-A-404470.

Preferably the cross-linked organic polymer particles have 5 the perfume trapped therein.

#### Polymers

It is a feature of this invention that the particles are composed of cross-linked organic polymeric material. Such 10 particles may be made from a variety of organic monomers, although in general these are olefinically unsaturated materials. Preparation may be by an emulsion polymerisation process, as will be explained further below.

15 It is also a feature of this invention that the particles have a mean diameter which is not more than 1μm. Particles of such small size can remain in colloidal suspension. As is known, particles of colloidal dimensions are kept in suspension by Brownian motion and by the effect of charges 20 on the particles surfaces, which cause the particles to repel each other and stay apart. Also, because the particles size is small in relation to the wavelength of light, they are generally not visible although they give an appearance of turbidity. Hence, a rinse conditioner 25 composition containing them can appear translucent.

There are three preferred techniques for the production of a polymer with perfume absorbed therein as herein described. These are as follows:

30

Method A, is to synthesise a polymer latex by emulsion polymerisation in the presence of the perfume. The monomers

used may include some polyfunctional monomer so as to produce cross-linking in the polymer. This enhances the strength and rigidity of the polymer. A low level of cross-linking provides the ability of particles to hold perfume.

5 Thus, there should desirably be cross linking between at least 0.5%, and 15% by number, of the total number of monomer residues present in the polymer and more preferably between 1% and 10%, e.g. between 1 and 5%, of the monomer residues. The polymer particle size range is preferably 10 between 50 and 200 nanometres.

Techniques for the production of a latex of small particles by emulsion polymerisation are well known. The polymerisation is normally carried out in the presence of a 15 surfactant which functions as an emulsifier. Raising the concentration of surfactant leads to smaller particle sizes, but does not generally lead to particle sizes smaller than 50 nanometres unless a special method, e.g. a microemulsion process, is used. Particle size is also 20 affected by temperature and hence rate of reaction, stirring speed and monomer/initiator ratio. Fast rates of polymerisation and higher stirring speeds lead to small particles. High proportions of monomer and low proportions of initiator favour the production of bigger particles.

25

After carrying out emulsion polymerisation it will generally be necessary to remove unreacted monomer. This will often be done by steam distillation, leading to some loss of perfume, although we have found that such losses of 30 perfume are acceptably small. Some monomers may be removed by chemical reaction to yield harmless or volatile products.

Method B: which is particularly preferred, is to commence with a pre-formed cross-linked polymer latex as a dispersion in liquid, e.g. water. The perfume is dissolved 5 in a low boiling organic solvent which is able to swell the polymer particles. The solution is brought into contact with the polymer latex, causing the polymer particles to swell and absorb the perfume. The solvent is then evaporated, leaving the perfume trapped in latex particles. 10 There should desirably be the same amount of cross-linking between of the monomer residues as in method A.

For method B, residual monomer can be removed from the polymer before the polymer comes into contact with the 15 perfume.

For either of these procedures the polymer should be capable of forming a colloidal emulsion in water. A latex of colloidal polymer particles will generally contain from 20 3% to 50% polymer, usually from 3% to 40%. Various polymerisation methods may be used for making polymers. Natural or modified natural polymers might also be used, e.g. a natural rubber latex.

25 Suitable monomers for radical addition polymerisation are those containing polymerisable olefinic unsaturation. Monomers which may be used include styrene, vinyl acetate, ethylene, propylene, vinyl pyrrolidone, vinyl chloride, acrylonitrile, methyl methacrylate, and other acrylates and 30 methacrylates. The monomers may be used either singly or in combination. Examples of polyfunctional monomers which may be used to effect cross-linking include divinyl benzene,

divinyl ether, ethyleneglycol dimethacrylate, penta-erythritol triacrylate and polyallyl sucrose. Suitable radical initiators include sodium or potassium persulphate, 2,2'-azobis-isobutyronitrile (AIBN) and 4,4'-azobis (4-5 cyanovaleric acid). A water soluble initiator is preferable. Polymerisation temperature is preferentially in the range 40-90°C.

For Method B, it is possible to use natural and modified 10 natural polymers, e.g. cellulose, modified cellulose, cellulose acetate, cellulose butyrate and hydroxy ethyl cellulose, as well as synthetic latices made from the polymers referred to above.

15 When Method A is used, the perfume should preferably be soluble in the monomer and compatible with the polymer. For Method B, the perfume should also be compatible with the polymer itself. This prevents phase separations which may cause problems.

20

The absorptions of perfume by polymer may be by absorption into open pores through capillary action, or by encapsulation or dissolution in the polymer so that release of perfume is by diffusion through the polymer, or it may 25 be adsorption onto the hydrophobic polymer material. More than one of these modes of absorption may occur at the same time.

A polymer with absorbed perfume may have the polymer and 30 the perfume in a weight ratio lying in the range from 25:1 to 2:1, especially 20:1 to 3:1.

The amount of polymer particles with absorbed perfume included in a rinse conditioning composition is preferably such an amount that the perfume is present in an amount from 0.1 to 10% by weight of the composition.

5

In many instances, the amount of polymer with absorbed perfume is likely to be such that its perfume amounts to 0.1% to 3%, or even 0.1% to 2% by weight of the composition.

10

A composition according to this invention may incorporate additional perfume which is not located or absorbed in or on the particles (i.e. it is outside the particles and not absorbed thereon) in addition to the perfume which is 15 absorbed onto or into such particles.

References herein to the amount of absorbed perfume in the particles is to be construed as the amount of perfume located in or on the particles, but not perfume separately 20 added to the composition.

If this is done, it can be arranged by choice of the amounts and nature of the perfumes which respectively are and are not absorbed onto the particles that the fragrance 25 on the fabrics after rinsing and drying will come principally from the perfume which was absorbed onto the porous particles whereas the apparent fragrance of the rinse conditioner composition will be principally attributable to the perfume which is not so absorbed. This 30 can enable the producer to control a difference in fragrance between the rinse conditioner composition and the fragrance of the fabrics after rinsing and drying.

It may therefore be desirable that the perfume which is not absorbed onto particles, which principally provides the fragrance of the rinse conditioner composition itself, does 5 not exhibit high substantivity towards the fabrics. It may also be desirable that the weight ratio of perfume which is and respectively is not absorbed or included in or on particles lies in a range from 10:1 to 1:4, especially from 10:1 or 4:1 to 1:1.

10

It may be arranged that the polymer melts when heated to ironing temperatures so that perfume which is absorbed onto the polymer particles is released and provides a perceptible fragrance during ironing. If this is desired it 15 will be appropriate for the organic polymer of the porous polymer particles to soften and flow at a temperature in the range from 100°C to 220°C (that is, to have a melting temperature lying in the range 100°C-220°C).

20 Choice of polymer characteristics can affect the ease with which perfume is released. Using monomers which give a more crystalline polymer, and incorporating cross-linking will both inhibit the release of the perfume, so that the perfume may be released more slowly over a longer period or 25 may be released when ironing melts the polymer.

It is preferred that there is cross-linking between at least 0.5% by number of the total number of monomer residues present. There may be cross-linking between up to 30 10% by number of the monomer residues, or possibly even more eg. up to 15% by number. Preferred is a range of 0.5%

or 1% up to 5% or 8% by number of the monomer residues in the polymer.

Other ingredients

5 Rinse conditioner compositions may contain a number of materials in addition to the fabric softening material, the porous particles and perfume. Materials which may be present include optical brightening agents, colourants, opacifiers, hydrotropes, viscosity control agents such as 10 electrolyte, stabilisers such as guar gum and polyethyleneglycol, anti-static agents and ironing aids. Silicones may be used for the latter purpose.

These various optional ingredients, if present in a rinse 15 conditioner, will generally not be present in amounts exceeding 5% by weight of the composition and they may well total not more than 10% by weight of the composition.

Rinse conditioner compositions in accordance with the 20 invention preferably have a pH of less than 6.0, more preferably a pH ranging from 2.0 to 5.0. Rinse conditioning compositions may contain pH-buffering agents such as weak acids and salts thereof, e.g. phosphoric, benzoic or citric acids and salts of these acids. The amount of buffering 25 material included in a composition may lie in the range from 0.5-10% by weight, preferably not more than 5% by weight.

Rinse conditioner compositions of this invention are 30 generally in the form of aqueous liquids which will generally contain at least 10%, usually at least 20% by weight water and often from 50% or 60% to 97% by weight of

water. Other product forms may be envisaged, however, including powders, creams, pastes, blocks or tablets. Suitable types of blocks and tablets are disclosed in European Patent Specification No. EP-A-255 779 (UNILEVER).

5 The ability of colloidal particles to remain in suspension is of course most relevant to products in liquid form.

In use compositions according to this invention are preferably added to a much larger volume of water to form a 10 liquor which is then used to contact the fabrics to be treated. Notably, such liquor can be formed by adding a composition by hand or by way of an automatic dispensing device to water in a washing machine.

15 One ingredient which is normally not included in rinse conditioning compositions is detergency builder. Generally speaking, rinse conditioning compositions in accordance with this invention will not contain ion exchange aluminosilicate builder, nor any other water-insoluble 20 inorganic material nor sodium tripolyphosphate nor any other water-soluble electrolyte in quantities greater than the quantity of the rinse conditioner material. It is likely that the compositions will be entirely free of tripolyphosphate and of any water-insoluble inorganic 25 materials.

The invention will now be further explained and illustrated by the following examples in which all amounts and percentages are by weight unless otherwise indicated.

Example 1

A cross-linked polystyrene latex with perfume absorbed therein was prepared by method A referred to above.

5 Polymerisation was carried out in a reaction vessel which was a round bottomed flask fitted with stirrer, nitrogen inlet tube and reflux condenser. The materials employed were:

10        styrene 8.8 gram  
              divinylbenzene (55% concentration) 0.17 gram  
              perfume 1 gram  
              cetyl trimethylammonium bromide (CTAB) 0.4 gram  
              polymerisation initiator 0.25 gram  
15        water 100 ml.

The CTAB was dissolved in most of the water (90ml) and the solution degassed. The perfume was dissolved in the styrene divinylbenzene mixture and the resulting solution was added 20 to the surfactant solution in the flask. After 10 minutes the initiator in the remaining water was added and the polymerisation reaction allowed to proceed for 6-8 hours while the contents of the flask were heated to 70°C. Emulsion polymerisation took place during this time giving 25 a latex consisting of a colloidal suspension of polymer particles in the water. The mean particle size was approximately 0.1 $\mu$ . Unreacted monomer was removed by steam distillation. This led to some loss of perfume, but about 90% of the perfume remained in the polymer latex.

A higher quantity of perfume could be incorporated into the latex particles by increasing the quantity of perfume, up to about 2.5 gram.

### 5 Example 2

In this example perfume was incorporated into performed latex in accordance with method B above.

A latex of cross-linked polystyrene particles of mean size 10 approximately  $0.1\mu$  was prepared using the following materials:

styrene 21.85 gram

divinylbenzene (55%) 4.85 gram

15 CTAB 0.13 gram

polymerisation initiator 0.33 gram

water 100 gram

The procedure was as given in Example 1 above and after the removal of excess monomer by steam distillation the solids content of the colloidal suspension was determined and found to be 7.8%.

A second stage used:

perfume 1 gram

25 CTAB 0.3 gram

dichloromethane 27 gram.

The perfume was dissolved in the dichloromethane solvent. This was then mixed with the CTAB and 50 grams of the latex 30 prepared as above. The heavy organic layer was dispersed throughout the mixture by shaking and then by application

of ultra-sound. This produced an opaque emulsion from which the solvent was removed using a rotary evaporator.

Example 3

5 A typical conditioner composition contains:

	<u>wt%</u>
Dimethyl di-hardened tallow	
10 ammonium chloride	5%
Cross-linked Polymer latex particles according to any of the preceding examples	sufficient to provide up to 0.4% perfume
15	
Demineralised water	balance to 100%
A chemical preservative could well be included, e.g. 0.02%	
by weight of 2-brom-2-nitropropane-1, 3-diol available	
20 under the Registered Trade Mark "Bronopol".	
An additional amount of the same perfume, or different, perfume as used in the latex particles can be included in conventional amounts.	
25	
To provide further examples the dimethyl di-hardened tallow ammonium chloride can be partially, or totally, replaced by 1,2-(hardened) ditallowyloxy-3-trimethyl ammonium propane chloride or a nonionic oily sugar derivative as described	
30 in the text above under nonionic compounds.	

Example 4

Several cross linked polymers latices with perfume incorporated in the latex particles were prepared using the methods A and B disclosed above and exemplified by Examples 5 1 and 2. Details of these various latices are given in the following Table 1 where percent solids denotes the percentage by weight of polymer in the aqueous latex; percent perfume denotes the quantity of perfume by weight as a percentage of the total weight of polymer and perfume.

10

Each latex was used to deliver perfume to fabric in accordance with the following procedure which used three fabrics namely 70-30 polyester/cotton, a bulked acrylic fabric and cotton terry towelling.

15

Six examples of each of the three fabrics were washed at 50°C using an unperfumed detergent composition containing anionic detergent, phosphate builder and other conventional detergent ingredients.

20

The wash load was rinsed twice with water only and spun dry. At this point the wash load was divided into two halves each containing three pieces of each fabric. One half of the wash load serving as a control was rinsed using 25 a rinse conditioning composition containing the same perfume as that used to make the latices. The other half of the wash load was rinsed using unperfumed rinse conditioning composition mixed with an amount of latex calculated to contain the same quantity of perfume. Each of 30 the halves of the wash load was spun dry, line dried, stored overnight and then assessed as follows.

The perfume intensity assessment was carried out by a panel of assessors trained to recognise the perfume and score the perfume intensity on a 0-5 scale as extending from 0 = no perfume perceptible through 5 - extremely strong perfume 5 perceived. The panellist's results were averaged and are set out in Table 1 below where "Δ intensity" denotes the amount by which the panellists' mean score exceeded their mean score for the control composition. The results are given in Table 1 below.

10

The two non-cross linked styrene monomer only examples are comparative.

Table 1

15 Monomers	Method	%Solids	%Perfume	ΔIntensity	Fabric
STY	B	9.6	20	0.9	Terry
				0.9	Polycotton
				0.6	Acrylic
20 STY/5% DVB	B	6.5	10	0.7	Terry
				0.8	Acrylic
				1.7	Terry
25	B	5.3	10	0.9	Polycotton
				1.2	Acrylic
				0.4	Terry
STY	A	12.3	10	0.5	Acrylic

30 From the above results it is demonstrated that the greater the level of DVB, the greater the level of cross-linking and the greater is the perfume substantivity/intensity.

Example 5

Several cross-linked polymer latices with perfume incorporated therein were prepared by the Method B above, exemplified in Example 2. Details are given in the following Table 3.

Table 2

Latex No.	Monomers %	Solids %	Perfume	Avge Particle size (μm)
10				
I	Styrene/DVB	22	20	0.10
II	Styrene/DVB	10	20	0.11
III	Styrene/DVB	23.3	10	0.10

These latices were used to deliver perfume to fabric, 15 either terry towelling or polyester cotton mixtures, using a similar procedure to that in the previous Example, or a variant procedure in which the fabric pieces were tumble dried at 70-75°C. The rinse conditioner contained 5% by weight cationic fabric softener (which was 20 dimethyldistearyl ammonium chloride). In some experiments the rinse conditioner contained sufficient latex to provide 0.25% by weight perfume. In other experiments the quantity of latex was halved, but compared with a control containing 0.25% by weight perfume. In other experiments the quantity 25 of latex was halved, but compared with a control containing 0.25% by weight of perfume.

Assessment of the dried fabric pieces was carried out as in Example 4 above, except that the results are expressed as 30 mean perfume scores, and not as  $\Delta$  relative to a control as in the previous tables.

Details of these experiments and the results obtained are given in the following Table 3.

Table 3

5

Mean Perfume Intensity Scores (0-5 Scale) On Dry Fabric

<u>Latex No:</u>	<u>Perfume Level in Composition</u>	<u>Fabric Type</u>	<u>Drying Regime</u>	<u>Mean Scores</u>
10 a)				
III	0.25%	Terry	Line	2.2
II	0.25%	Terry	Line	1.9
I	0.25%	Terry	Line	2.0
None (perfumed	0.25%	Terry	Line	1.1
15 control)				
b)				
II	0.25%	Polycotton	Line	1.8
I	0.25%	Polycotton	Line	1.6
20 None (perfumed	0.25%	Polycotton	Line	1.1
control)				
c)				
III	0.125%	Terry	Line	1.2
25 I	0.125%	Terry	Line	1.2
None (perfumed	0.25%	Terry	Line	1.2
control)				
III	0.125%	Terry	Tumbled	1.8
I	0.125%	Terry	Tumbled	1.2
30 None (perfumed	0.25%	Terry	Tumbled	1.2
control)				

The results in the above table show that when the perfume levels are equal (at 0.25%) the perfume intensity retained

on the fabric after line drying is greater when the perfume is carried by polymer particles.

The experiments in which the latex provided 0.125% perfume 5 achieved a retention of perfume which was approximately equal to a control using double the quantity of perfume without latex.

Example 6

10 A fabric softening composition was prepared containing 20% by weight of 1, 2-ditallowyloxy-3-trimethyl ammonium propane chloride.

The suspension was a mobile white emulsion.

15

0.5% by weight of perfume was added to this composition. It thickened to such an extent as to become an immobile solid.

The same emulsion was mixed with a latex which was the 20 cross-linked latex I of Example 5. The amount was sufficient to provide 1% by weight perfume in the composition. The emulsion remained very mobile.

The same emulsion was mixed with (1) the same latex in an 25 amount sufficient to provide 0.5% by weight of perfume plus (ii) 0.5% by weight of perfume which was not included in a latex. Again the emulsion thickened dramatically to an immobile solid.

Example 7

A linear polymeric latex was prepared in the presence of perfume as a comparative example (7A). The materials employed were:

5

	n-butyl acrylate	140g
	N,N'-dimethylaminoethyl acrylate	4.3g
	polyoxyethylene (30) nonylphenyl ether	38.0g
10	perfume	36.1g
	polymerisation initiator	1.2g
	deionised water	500 ml

Polymerisation was carried out in a similar apparatus to 15 that of Example 1. The nonionic surfactant and the polymerisation initiator were dissolved in the water which was then degassed, after which it was stirred and heated to 62°C. The two acrylate monomers were mixed with the perfume and the resulting solution was added drop-wise to the water 20 over a period of two hours. The polymerisation reaction was allowed to continue for a further 7 hours while the contents of the flask were stirred at the same temperature of 62°C. After this the mixture was stem distilled to remove most of the residual monomer. The resulting latex 25 was then concentrated on a rotary evaporator reducing its volume by about 50% and in doing so removing remaining monomer to provide an odourless latex which was filtered through glass wool. 503g of a latex of 37 wt% solids content and 0.11 $\mu$ m average particle size was obtained.

30

A cross-linked polymeric latex was prepared using the following materials (example 7B):

n-butyl acrylate	140 g
N,N'-dimethylaminoethyl acrylate	4.3 g
ethylene glycol di(methylacrylate) (EGDMA)	6.0 g
cetyl trimethyl ammonium bromide (CTAB)	30 g
5 Polymerisation initiator	1.2 g
deionised water	500 ml

Polymerisation was carried out in a similar manner to that above. The CTAB was dissolved in the water, along with the initiator. The three acrylate monomers were mixed together 10 before addition. The EGDMA then functioned as a cross-linking agent. The latex obtained had a particle size of approximately 0.1μ.

36.1 grams perfume was incorporated into the resulting 15 latex in accordance with the procedure described in Example 2 above.

The linear and cross-linked latices prepared above (Examples 7A and 7B respectively) were used to incorporate 20 perfume into a rinse conditioner composition containing 5% by weight of dimethyl distearyl ammonium chloride as in Example 6. The amount of each latex was calculated so as to introduce 0.25% perfume in the rinse conditioner composition assuming that all perfume used in the 25 preparation of the latex has been retained in the latex. The resulting rinse conditioner compositions were compared with a composition containing the same fabric softener and 0.25% by weight perfume without latex.

30 Terry cotton test pieces were agitated in 1 litre of water containing 2 grams of the rinse conditioner under test. After agitation for 5 minutes the cloths were hand wring,

rinsed in a further litre of plain water for two minutes, then wrung again and line dried overnight. As in Example 4 a panel of assessors scored the perfume intensity on the dried cloths on a scale extending from

5 0 = no perfume perceptible through to  
5 = extremely strong perfume perceived

The results of this comparison and a subsequent repetition of it are set out in the following Table 4.

10

TABLE 4 COMPARISON OF LINEAR AND CROSSLINKED POLYMER LATTICES AS PERFUME CARRIERS

SAMPLE	EXPT 1	EXPT 2
Free perfume (control)	0.5	0.7
perfume I cross-linked latex (Example 7B)	1.4	1.2
perfume in linear latex (Example 7A)	1.0	0.9

15 As can be seen from the results above, the perfume incorporated in the cross-linked latex was more perceptible than either of the free perfume control or the perfume incorporated in the linear latex. These results are statistically significant at a 95% confidence level.

20

Using the same test procedure, a comparison was made between latex III of Example 5, the above cross-linked latex based on butyl acrylate (Example 7B) and perfume without latex. As before, the amount of each latex added to 25 the rinse conditioner composition was calculated so as to introduce 0.25% perfume. Some of the test cloths were

ironed before assessment. The results are set out in the following Table 5.

TABLE 5

SAMPLE	EXPT 1	EXPT 1 IRONED	EXPT 2	EXPT 2 IRONED
free perfume (control)	1.0	0.8	0.7	0.6
cross-linked styrene latex (Example 5 III)	2.2	3.1	1.6	2.8
cross-linked butyl acrylate latex (Example 7B)	1.5	1.3	1.3	1.6

5

As can be seen from this Table, both cross-linked latices provided an increase in the perceptibility of the perfume delivered to the fabric. This was particularly apparent with the cross-linked styrene latex after the test cloths 10 had been ironed.

**Claims**

1. A composition for use in the rinsing of laundry containing particles with perfume located or absorbed in or on the particles, characterised in that the particles are formed of cross-linked organic polymeric material and have a mean particle size not greater than 1 micron.
2. A composition according to claim 1 wherein the polymeric material and the perfume are in a weight ratio lying in the range from 25:1 to 2:1.
3. A composition according to claim 1 or claim 2 which is a rinse conditioner composition containing a material effective to soften fabrics.
4. A composition according to claim 3 which contains from 0.5 to 90% by weight of the fabric softening material and contains the particles in such amount that the perfume therein or thereon is from 0.1 to 10% by weight of the composition
5. A composition according to any preceding claim which is in the form of an aqueous liquid.
6. A composition according to claim 4 which contains from 0.5 to 40% by weight of the fabric softening material and contains the particles in such amount that the perfume therein or thereon is from 0.1 to 3% by weight of the composition.

7. A composition according to claim 6 which is a liquid composition containing at least 50% by weight of water.
8. A composition according to any one of claims 3 to 7 containing at least 12% by weight of the fabric softening material.
9. A composition according to any one of claims 3 to 8 wherein the fabric softening material is cationic and is an organic compound containing nitrogen and at least one hydrocarbon chain of 6 to 50 carbon atoms.
10. A composition according to any one of claims 3 to 9 containing from 0.5 to 90% by weight of fabric softening material which is cationic.
11. A composition according to any one of claims 3 to 10 wherein the amount of fabric softening material which is cationic is a majority of the fabric softening material present.
12. A composition according to any one of the preceding claims wherein the particles have the perfume trapped therein.
13. A composition according any one of the preceding claims wherein there is cross-linking between at least 0.5% by number of the total number of monomer residues present in the polymer.

14. A composition according to any one of the preceding claims which contains additional perfume which is outside the particles, the amounts of perfume which are and are not included in or on the particles lying in a weight ratio from 10:1 to 1:4.
15. A composition according to any one of the preceding claims wherein the particles are composed of organic polymer with a melting temperature lying in a range from 100°C to 220°C.
16. A method of treating laundry comprising contacting said laundry with a composition as defined in any one of claims 1 to 15.
17. A method of making a rinse conditioner comprising mixing;
  - (i) a fabric softening material and
  - (ii) particles of cross-linked organic polymeric material with a mean particle size not greater than 1 micron and with perfume located or absorbed therein of thereon.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 00/03279

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C11D3/50 C11D3/37		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 7 C11D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) WPI Data, EPO-Internal, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 617 051 A (ALLIED COLLOIDS LTD) 28 September 1994 (1994-09-28) cited in the application	1-3, 12, 16, 17
A	page 6, line 7 - line 14; claim 1; example 6	4-11, 13-15
A	WO 98 28396 A (QUEST INTERNATIONAL B.V.) 2 July 1998 (1998-07-02) cited in the application claims 1, 10; examples 6, 7	1-17
A	EP 0 397 245 A (PROCTER & GAMBLE) 14 November 1990 (1990-11-14) claim 1; example VI	1-17
A	EP 0 385 534 A (PROCTER & GAMBLE) 5 September 1990 (1990-09-05) claims 1, 2, 8; table 2	1-17
<input type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.
* Special categories of cited documents :		
*A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed		
*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *&* document member of the same patent family		
Date of the actual completion of the international search	Date of mailing of the international search report	
10 August 2000	22/08/2000	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  Saunders, T

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

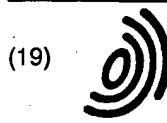
PCT/EP 00/03279

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0617051	A 28-09-1994	AT 121427 T AU 2269488 A DE 3853604 D DE 3853604 T DK 188589 A EP 0305139 A EP 0330692 A ES 2070854 T FI 891918 A WO 8901948 A JP 2500598 T NO 891651 A		15-05-1995 31-03-1989 24-05-1995 31-08-1995 20-06-1989 01-03-1989 06-09-1989 16-06-1995 21-04-1989 09-03-1989 01-03-1990 20-06-1989
WO 9828396	A 02-07-1998	AU 5331798 A AU 5331898 A AU 5331998 A EP 0950087 A EP 0950088 A EP 0950070 A WO 9828398 A WO 9828339 A US 6024943 A		17-07-1998 17-07-1998 17-07-1998 20-10-1999 20-10-1999 20-10-1999 02-07-1998 02-07-1998 15-02-2000
EP 0397245	A 14-11-1990	AT 118244 T AU 644357 B AU 5491290 A BR 9002233 A CA 2015736 A CN 1047336 A,B CN 1101071 A DE 69016695 D DE 69016695 T DK 397245 T EG 19472 A ES 2067647 T GR 3015030 T IE 66114 B JP 3033196 A MX 172021 B NZ 233580 A PT 94004 A,B TR 24664 A		15-02-1995 09-12-1993 29-11-1990 13-08-1991 11-11-1990 28-11-1990 05-04-1995 23-03-1995 13-07-1995 03-04-1995 29-06-1995 01-04-1995 31-05-1995 13-12-1995 13-02-1991 29-11-1993 26-03-1993 08-01-1991 01-03-1992
EP 0385534	A 05-09-1990	US 4946624 A AT 104378 T AU 640631 B AU 5016490 A CA 2009046 A,C DE 69008005 D DE 69008005 T DK 385534 T EG 18844 A ES 2063241 T IE 63881 B JP 2277889 A NZ 232679 A PT 93225 A,B TR 27391 A		07-08-1990 15-04-1994 02-09-1993 30-08-1990 27-08-1990 19-05-1994 18-08-1994 08-08-1994 29-09-1994 01-01-1995 14-06-1995 14-11-1990 25-09-1992 31-08-1990 03-02-1995

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0385534 A	US 5126061 A	30-06-1992	



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 925 776 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:  
29.08.2001 Bulletin 2001/35

(51) Int Cl.7: A61K 7/46, A61K 7/32,  
A61L 9/04

(43) Date of publication A2:  
30.06.1999 Bulletin 1999/26

(21) Application number: 98123628.4

(22) Date of filing: 10.12.1998

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE

Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 16.12.1997 EP 97122122

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(54) Polymer with binding capacity for organoleptic substances

(57) The invention relates to a polymer presenting binding sites for at least one organoleptic substance, and specifically, which binding sites are at least partly molecularly imprinted with an organoleptic substance. The polymer which has the property to bind specific classes of organoleptic molecules can be used in any

application where a long lasting effect of the organoleptic substance is targeted, e.g. in cosmetic products, deodorants, air refreshing products, laundry products and in fibers for fabrics. If the polymer prior has been imprinted with malodor molecules this polymer is used to reduce malodor.

EP 0 925 776 A3



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 98 12 3628

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)						
A,D	MULDOON ET AL.: "Plastic antibodies..." CHEMISTRY & INDUSTRY, 18 March 1996 (1996-03-18), pages 204-207, XP001010094 * page 205, paragraph 2 * * figure 3; table 1 * -----	1-29	A61K7/46 A61K7/32 A61L9/04						
A	NORRLÖW ETAL.: "Acrylic polymer preparations containing recognition ..." JOURNAL OF CHROMATOGRAPHY, vol. 299, 1984, pages 29-41, XP002936912 * page 33, paragraphs 1,2; figure 1; table 1 *	1-29							
A	WO 97 38015 A (IGEN INC. ET AL.) 16 October 1997 (1997-10-16) * claims 1,4-7,12-17 * -----	1-29							
A	US 5 630 978 A (DOMB ) 20 May 1997 (1997-05-20) * column 5, line 41 - column 11, line 38 * -----		TECHNICAL FIELDS SEARCHED (Int.Cl.)						
			A61K A61L C11D A23L						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>BERLIN</td> <td>3 July 2001</td> <td>Alvarez Alvarez, C</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background C : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>				Place of search	Date of completion of the search	Examiner	BERLIN	3 July 2001	Alvarez Alvarez, C
Place of search	Date of completion of the search	Examiner							
BERLIN	3 July 2001	Alvarez Alvarez, C							

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 98 12 3628

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

03-07-2001

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9738015 A	16-10-1997	AU	2721797 A	29-10-1997
US 5630978 A	20-05-1997	AU	5776396 A	30-12-1996
		WO	9640822 A	19-12-1996
		US	5858296 A	12-01-1999

EPO FORM P049  
For more details about this annex : see Official Journal of the European Patent Office, No. 12/82